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FORM PTO-1390 (REV 5-93) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
225/50412

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)
09/937377

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/01914	04 March 2000	23 March 1999

TITLE OF INVENTION
PROCESS FOR PRODUCING A CATALYTIC CONERTER

APPLICANT(S) FOR DO/EO/US
BERGINGER, Andreas; BRITZ, Peter, DAHLHOFF, Ellen; HÖLDERLICH, Wolfgang; SCHNEIDER, Martin; STÄB, Gabriele; and URBAN, Peter

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US)
6. [X] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unexecuted).
10. [X] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Item 11. to 16. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [X] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:

Copies of (1) First page of int'l pub. No. WO 00/56452; (2) International Search Report; (3) International Preliminary Examination Report; and annexes (4) Form PCT/IB/308; (5) 5 sheets formal drawings.

23911
PATENT TRADEMARK OFFICE

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/937377	INTERNATIONAL APPLICATION NO. PCT/EP00/01914	ATTORNEY'S DOCKET NUMBER 225/50412

17. [X] The following fees are submitted:				CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO $860.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) $690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2) $710.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37CFR 1.445(a)(2) paid to USPTO $1000.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than [ ] 20 [x] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$ 130.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	13-20=	0	X $18.00	$ 0	
Independent Claims	1-3=	0	X $80.00	$ 0	
Multiple dependent claims(s) (if applicable)			+ $270.00	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 990.00	
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$ 0	
SUBTOTAL =				$ 990.00	
Processing fee of $130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0	
TOTAL NATIONAL FEE =				$ 990.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). $40.00 per property +				$ 0	
TOTAL FEE ENCLOSED =				$ 990.00	
				Amount to be: refunded	$
				charged	$

a. [X] A check in the amount of $ 990.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. ______ in the amount of $______ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees, which may be required, or credit any overpayment to Deposit Account No. 05-1323 (225/50412). A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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32,390
REGISTRATION NUMBER

September 24, 2001
DATE

Attorney Docket: 225/50412
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Andreas Berginger et al.

Serial No.: Not Yet Assigned Int'l Appln. No.: PCT/EP00/01914

Filed: September 24, 2001 I.A. Filing Date: March 4, 2000

Title: PROCESS FOR PRODUCING A CATALYTIC CONVERTER

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly enter the following amendments to the English language translation of the international PCT application identified above prior to examination.

Please substitute the new Abstract of the Disclosure attached as Appendix I for the Abstract appearing on the last page of the translation.

Please replace pages 1-11 of the translation with the substitute specification attached as Appendix II.

Please cancel claims 1-16 of the translation and add the following new claims:

--17. A process for producing a catalytic converter, in which catalytically active material is deposited on a substrate as a porous or non-cohesive layer, as a result of the substrate being immersed in an electrolyte which contains the catalytically active material and voltage being applied between

the substrate and a counterelectrode, comprising:

depositing the catalytically active material on a metallic substrate, and

applying an electric direct voltage, on which an alternating voltage is superimposed in such a way that the sign of the sum voltage of direct and alternating voltage does not change, between the substrate and the counterelectrode.

18. The process according to Claim 17, wherein the direct voltage at least corresponds to the deposition potential of the catalytically active material.

19. The process according to Claim 17, and further comprising providing the substrate, on its surface which is to be coated, with a predetermined surface roughness prior to the deposition.

20. The process according to Claim 19, wherein the surface roughness is in the range from 0.3 μm to 10 μm.

21. The process according to Claim 17, wherein the catalytically active material is deposited as substantially spherical metal clusters as a result of the alternating voltage component being applied with a frequency of over 50 Hz.

22. The process according to Claim 17, wherein the catalytically active material is deposited as substantially

dendritic metal clusters as a result of the alternating voltage component being applied with a frequency of between 5 and 50 Hz.

23. The process according to Claim 17, wherein the catalytically active material is a precious metal, a mixture of precious metals or catalytically active materials, or a mixture of precious metals and catalytically active materials.

24. The process according to Claim 17, wherein said metallic substrate is a stainless steel substrate, and wherein substantially spherical platinum clusters are deposited on said stainless steel substrate from a solution of a platinum compound in 0.1 M H_2SO_4 with a platinum content of approximately 0.1 g/l as a result of a modulated voltage, comprising said direct voltage of approximately 1.3 volts superimposed with said alternating voltage with a voltage swing of 0.3-1 volt and a frequency of 50-100 Hz, being applied between said stainless steel substrate and said counterelectrode.

25. The process according to Claim 17, wherein said metallic substrate is a stainless steel substrate, and wherein substantially dendritic platinum clusters are deposited on said stainless steel substrate from a solution of a platinum compound in 0.1 M H_2SO_4 with a platinum content of approximately 0.1 g/l as a result of a modulated voltage, comprising said direct voltage of approximately 1.3 volts superimposed with said alternating voltage with a voltage swing of 0.3-1 volt and a

frequency of 5-15 Hz, being applied between said stainless steel substrate and said counterelectrode.

26. The process according to Claim 17, wherein said metallic substrate is a stainless steel substrate, and wherein substantially dendritic rhodium clusters are deposited on said stainless steel substrate from a solution of a rhodium compound in 0.1 M H_2SO_4 with a rhodium content of approximately 0.2 g/l as a result of a said direct voltage of 1.4-1.6 volt applied between said stainless steel substrate and said counterelectrode and said alternating voltage (V_{ac}) with a voltage swing (V_{PP}) of 0.3-1.5 volts and a frequency of 5-15 Hz being superimposed.

27. The process according to Claim 24, wherein the platinum clusters have sizes between 2 nm and 1 µm.

28. The process according to Claim 17, wherein the counterelectrode is formed by platinum-coated titanium.

29. The process according to Claim 25, wherein the platinum clusters have sizes between 2 nm and 1 µm.--

REMARKS

This Preliminary Amendment is being filed in order to incorporate specification and claim amendments reflected in the annexes to the International Preliminary Examination Report into the present U.S. national stage application, to improve the form of the specification and abstract, and to place the claims of this U.S. national stage application into a form which is more appropriate for examination in the United States.

A marked-up version of the substitute specification, showing matter added to the translation by underlining and matter deleted from the translation between brackets, is attached to the Preliminary Amendment as Appendix III. The substitute specification is believed to contain no new matter.

Respectfully submitted,

September 24, 2001

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New page 1

Process for producing a catalytic converter

The invention relates to a process for producing a catalytic converter.

The disclosure JP-A-08 134 682 has described an electroplating process for coating a metallic substrate with a smooth precious metal layer, in which an iron-containing substrate is provided with a platinum covering. The patent DE 197 32 170 C2 has disclosed a process for covering a ceramic SiC substrate in a locally selective manner with a platinum covering, the surface of which matches the rough ceramic surface, as a result of a direct voltage being applied between the substrate and a counterelectrode. The coated substrate is then treated at elevated temperature of over 400°C.

EP-A-106 197, which forms the starting point for the invention, has disclosed a process for the electrochemical deposition of a porous platinum layer. The layer is deposited on a carbon or semiconductor substrate. In this process, a one-off high voltage pulse is applied between substrate and counterelectrode, so that nuclei are deposited on the substrate. There then follows a prolonged pulse at a lower voltage, during which growth of the nuclei takes place. US-A-4,273,624 has disclosed an electroplating process in which a thin, continuous layer of platinum is deposited on an SnO_2 substrate. JP-A-7 80 327 has disclosed a catalytic converter in which a metallic substrate is coated with a thin, non-porous layer of precious metal. The lack of pores means that the catalytic converter is distinguished by a high resistance to oxygen.

Additional page 1a

The object of the invention is to provide a process for coating a metallic substrate which allows the deposition of a precious metal with a large surface area and good adhesion to a substrate.

This object is achieved by the features of the independent claim.

According to the invention, a layer of catalytically active metallic material is deposited on a metal substrate by means of electrochemical deposition, the substrate being immersed in an electrolyte which contains the catalytically active metallic material

catalytically active material being deposited on the substrate as a porous or non-cohesive layer.

It is particularly advantageous for the substrate to be provided, on its surface which is to be coated, with a predetermined surface roughness prior to the deposition, the surface roughness preferably lying in the range from 0.3 µm to 10 µm. A further preferred range for the surface roughness is between 0.3 µm and 3 µm. The surface roughness is expediently generated by thermal and/or mechanical and/or chemical treatment.

The catalytically active material is preferably formed from metal clusters with a diameter of between 2 nm and 1 µm, preferably between 2 nm and 300 nm.

The particular advantage of the process is that it is possible to deposit catalytically active layers with a very large surface area and a relatively low level of catalytically active material. The layers exhibit good adhesion and are stable at high temperatures even after prolonged use.

Preferred catalytically active materials are precious metals. One suitable catalytically active material is platinum. A preferred counterelectrode is formed by platinum-coated titanium sheet. A further preferred counterelectrode consists of platinum-coated nickel.

In a particularly preferred refinement of the invention, platinum is deposited with different morphologies. This provides catalytic converters which have different selectivities for conversion of matter. For example, it is possible to produce a preferred platinum catalytic converter for a reforming reactor which, despite a high carbon monoxide concentration in an H_2/CO mixture, has a continuously high activity for hydrogen conversion in operation.

Further advantages and configurations of the invention will emerge from the further claims and the description. The invention is described in more detail below with reference to a drawing, in which:

Figure 1 shows an outline view of a structure for carrying out the process according to the invention,

Figure 2 diagrammatically depicts a section through a coated surface,

Figures 3a, b show two scanning-electron microscope images of the surface of a catalytic converter with dendritic platinum clusters,

Figure 4 shows a scanning-electron microscope image of the surface of a catalytic converter with spherical platinum clusters,

Figures 5a, b show two scanning-electron microscope images of the surface of a catalytic converter with dendritic platinum clusters before (Figure 5a) and after (Figure 5b) a long-term test,

Figures 6a, b show a comparison of rough (Figure 6a) and smooth (Figure 6b) surface profiles of steel substrates prior to the coating with catalyst material,

Figure 7 shows a measurement curve indicating the hydrogen conversion achieved by a catalytic converter with spherical platinum clusters in a CO-containing atmosphere, and

Figure 8 shows a measurement curve illustrating the conversion of hydrogen achieved by a catalytic converter with dendritic platinum clusters in a CO-containing atmosphere.

Figure 1 shows an arrangement for carrying out the process according to the invention. A function generator 1 generates a modulated voltage which is amplified in an amplifier 2 and is applied between an anode 3 and a substrate 4 which is to be coated in a deposition bath 5. A direct voltage V_{dc} is preferably superimposed with an alternating voltage V_{ac}. The sum voltage of direct voltage V_{dc} and alternating voltage V_{ac} is also referred to below as the modulated voltage V_m. The alternating voltage is expediently sinusoidal, but may also adopt other forms, for example sawtooth or square-wave form.

The catalytically active material 6 is deposited on the substrate 4 in the form of clusters. According to the invention, the clusters may have different forms which can be predetermined by the deposition parameters. The substrate 4 which is coated with catalytically active material 6 then forms the catalytic converter.

The direct voltage V_{dc} is preferably at least as great as the deposition potential of the catalytically active material 6 on the substrate 4, particularly preferably at most 50% higher. The precise level of the direct voltage V_{dc} is dependent on the constituents and process conditions employed and may, for example, adopt different values for differently pretreated substrates, although these values do not usually differ greatly from one another. When depositing mixed systems as catalytically active material, it is also possible for the preferred direct voltage V_{dc} to lie below this deposition potential.

Stainless steel, particularly Cr-Ni steel 1.4541 or CR-Ni steel 1.4571 or Cr-Al steel 1.4767 is used as a particularly suitable substrate. It is expedient for the substrate to be sand-blasted or roughened in some

other way, for example chemically, and to undergo alkaline degreasing prior to the coating. This improves the adhesion of the catalytically active material 6 to the substrate 4.

In a preferred embodiment, the alternating voltage V_{ac} has a maximum voltage swing V_{PP} between minimum and maximum which is lower than the direct voltage V_{dc}, so that overall the sign of the sum voltage between substrate 4 and counterelectrode 3 does not change.

The current between substrate 4, which serves as the cathode during the deposition, and anode 3 is recorded and, in accordance with Faraday's law, is used as a measure for determining the quantity of catalytically active material 6 deposited, this material being contained in the deposition bath; current contributions which flow for the purpose of building up and breaking down the electrolytic double layer on account of the modulation are expediently eliminated, since they do not originate from the reduction or oxidation of cations or anions.

It is preferable to deposit precious metals in order to produce the catalytic converter. However, it is also possible to deposit mixtures of precious metals. An expedient, inexpensive anode is platinum-coated titanium instead of a standard sacrificial anode made from solid platinum, which can be used to particularly good effect if platinum is to be deposited as catalytically active material. However, other precious metals and also other metals can be deposited in this inventive way.

The frequency and/or the amplitude V_{PP} and/or the voltage offset V_{dc} of the modulated voltage can be adjusted in order to optimize the deposition parameters for the particular system. The values affect both the

size of the clusters which are deposited on the metallic cathode and their morphology. Overall, the clusters on the substrate 4 constitute a large active surface area for catalytic reactions. The optimum cluster size can be set in each case for different applications by suitably selecting the deposition parameters and the duration of coating.

It is particularly advantageous for the surface of the substrate 4 which is to be coated to be roughened prior to the coating, for example by pickling or sand-blasting. Other methods for increasing the surface roughness are also possible. This is illustrated in Figure 2 with reference to a diagrammatic side view of a coated surface. A substrate 4 has a roughened surface 4.1 on which spherical metal clusters 6.1 are arranged in recesses. The metal clusters 6.1 may also be deposited on the peaks or the flanks of the roughened areas.

The increased surface roughness has the advantage that deposited clusters 6.1 adhere more successfully to the substrate surface, and undesirable combining of the clusters 6.1 is suppressed. A catalytically active layer of individual clusters 6.1 is formed; the layer is preferably not continuous, but rather is formed from isolated clusters 6.1.

The surface roughness is preferably between 0.3 μm and 10 μm, particularly preferably between 0.3 μm and 3 μm. A large active surface area is formed from the finely distributed clusters 6.1. A further advantage is that the increased surface roughness even also contributes to increasing the surface area of the substrate 4 and therefore also the chemically active surface area. At the same time, the clusters 6.1 can be very small, so that overall only a small quantity of the expensive catalytically active material 6 has to be deposited,

yet at the same time the catalytic converter is distinguished by a high catalytic activity.

The adhesion of the metallic clusters 6.1 to the substrate surface 4.1 is very good. This makes the catalyst layer more resistant to erosion.

A particular advantage over conventional catalyst layers is that, according to the invention, good heat transfer from the catalyst layer to the substrate 4 is possible, since metallic clusters 6.1 are joined to a metallic substrate 4. By contrast, known, conventional catalyst layers are produced, for example, with supported catalyst materials, in which ceramic support particles are coated with a precious metal. In this case, the heat transfer between catalytically active precious metal and a substrate is significantly worse, since the ceramic particles arranged between them have only a low thermal conductivity. In addition, in a catalytic converter which is produced according to the invention, it is also possible to dispense with standard adhesion promoter layers, which have an additional adverse effect on the heat transfer properties between catalytically active material 6, 6.1 and substrate 4.

A substrate 4 which is coated according to the invention is therefore particularly suitable for use as an oxidation catalytic converter for treating exhaust gases in fuel cell systems. A further expedient application is for various heterogeneously catalysed processes. The catalytic converter according to the invention and the process according to the invention are particularly advantageous in exhaust-gas catalytic converters for vehicles.

Figure 3 shows scanning-electron microscope images of preferred catalytic converters with dendritic platinum

clusters (Figures 3a, 3b), and with rhodium clusters which are of substantially dendritic form.

Dendritic platinum clusters are preferably deposited on a stainless steel substrate as a result of a direct voltage V_{dc} of 1.4 volts being superimposed with an alternating voltage V_{ac} with V_{PP}=0.75 volt (peak-peak voltage swing) and the modulated voltage being applied between a stainless steel substrate and a counterelectrode. The frequency of the alternating voltage V_{ac} is 10 Hz. The electrolyte used is platinic acid, in particular hexachloroplatinic acid, with a platinum content of 0.1 g/l. The deposition preferably takes place at room temperature.

The platinum clusters present dendritic growth, and no spherical platinum clusters are observed. The preferred catalytic converter has a high level of activity for hydrogen conversion even in the presence of carbon monoxide, carbon monoxide also being converted with a good yield at the same time.

In the selected system, dendritic platinum clusters are deposited with frequencies of between 5 and 15 Hz and an alternating voltage V_{ac} with a voltage swing V_{PP} of between 0.3-1 volt.

A further preferred catalytic converter is produced by deposition of rhodium on stainless steel, preferably comprising stainless-steel sheet 1.4541 or 1.4571 or 1.4767. It is also possible for mixed catalysts of platinum to be deposited in this way or to deposit catalysts comprising mixtures of precious metals and/or catalytically active materials, such as for example PtRh, PtRu, PdPt.

Deposition takes place from a solution of 0.2 g/l of rhodium in 0.1 M H_2SO_4 at room temperature with a direct

voltage V_{dc} of 1.4-1.6 volts and a superimposed alternating voltage V_{ac} with V_{PP}=1 volt (peak-peak amplitude) and a frequency of 10 Hz. The formation of dendritic growth of the clusters can be improved still further by varying the voltage parameters.

A catalytic converter of this type has a good activity for methanol. A catalytic converter of this type is therefore particularly suitable for use in fuel cell vehicles operated with methanol, particularly preferably in catalytic burners.

Figure 4 shows a scanning-electron microscope image of a further preferred catalytic converter with spherical platinum clusters. The deposition takes place using a direct voltage V_{dc} of 1.2-1.4 volts and an alternating voltage V_{ac} with V_{PP}=0.4 volt and 100 Hz; the deposition bath otherwise corresponds to that used for Figure 3.

In this system, an alternating voltage V_{ac} with frequencies of more than 50 Hz, preferably up to 150 Hz, is preferably used for the deposition of spherical platinum clusters. The direct voltage V_{dc} which is applied varies with the substrate pretreatment and, for the deposition of spherical clusters, is substantially equal to or tends to be slightly lower than that used for the deposition of dendritic clusters.

Figure 5 shows a comparison of scanning-electron microscope images of a catalytic converter with dendritic platinum clusters before (Figure 5a) and after (Figure 5b) a long-term test, in which the catalytic converter was exposed to an H_2/CO mixture at high temperature for more than 200 h. Although exposed to high temperatures of up to 600°C, the porous or non-cohesive platinum layer as catalyst remains stable; the clusters remain fixed in position and do not converge.

The layer which has been deposited in accordance with the invention demonstrates that the clusters in practice do not change before and after long-term use.

Figure 6 shows a comparison of rough (Figure 6a) and smooth (Figure 6b) surface profiles of steel substrates which have been used for the deposition of the platinum. The adhesion of the platinum clusters to the roughened substrate is significantly better than the adhesion to the smooth substrate; the layers are wipe-resistant, while the layers on an untreated, smooth substrate are not wipe-resistant. The surface roughness is preferably between 0.3 µm and 10 µm, particularly preferably between 0.3 µm and 3 µm.

The catalytic activity and/or selectivity of the catalytic converter differs depending on the particular form of the clusters. A preferred catalytic converter with spherical platinum clusters converts hydrogen in a substantially selective manner. The catalytic converter is poisoned and has a greatly reduced activity in the presence of carbon monoxide. A catalytic converter of this type is preferably used under carbon monoxide-free conditions.

By contrast, a preferred catalytic converter with dendritic platinum clusters firstly has a high tolerance to carbon monoxide during the hydrogen conversion and secondly has a high selectivity and high activity both for the hydrogen conversion and for the carbon monoxide conversion.

Figure 7 shows a measurement curve illustrating the hydrogen conversion achieved by a preferred catalytic converter with spherical platinum clusters. The catalytic converter is exposed to an H_2/CO mixture under standard operating conditions. After even a few

minutes, the hydrogen conversion in the presence of CO falls to low levels.

Figure 8 shows a measurement curve illustrating the hydrogen conversion achieved by a preferred catalytic converter with dendritic platinum clusters. In this case too, the catalytic converter is exposed to an H_2/CO mixture under standard operating conditions. However, the measurement curve shows that the conversion of hydrogen and for carbon monoxide remains at substantially constant high levels over more than 200 hours. The conversion can in each case be improved further, since the operating conditions have not been optimized.

A catalytic converter which has been produced in accordance with the invention is particularly resistant to erosion, and its production can be successfully reproduced. The deposition parameters of the catalytically active material on the substrate can easily be optimized for different materials which are to be deposited by suitably selecting the direct voltage V_{dc}, alternating voltage amplitude V_{PP} and/or frequency. Process control is simple, and the catalytic converter properties can be reproducibly set by simple modifications to the deposition process. The yield of material is good, so that, for example for highly active platinum catalytic converters, relatively small quantities of the precious metal have to be used.

A preferred use for a catalytic converter produced according to the invention is use in a CO-rich environment, in particular in an exhaust-gas cleaning system in a motor vehicle. A further preferred use of a catalytic converter according to the invention is its use in a fuel cell system.

Patent Claims

1. Process for producing a catalytic converter, in which catalytically active material (6, 6.1) is deposited on a substrate (4) as a porous or non-cohesive layer, as a result of the substrate (4) being immersed in an electrolyte (5) which contains the catalytically active material (6) and voltage being applied between the substrate (4) and a counterelectrode (3), characterized in that the catalytically active material (6, 6.1) is deposited on a metallic substrate (4), and in that an electric direct voltage (V_{dc}), on which an alternating voltage (V_{ac}) is superimposed in such a way that the sign of the sum voltage of direct and alternating voltage (V_{ac}, V_{dc}) does not change, is applied between substrate (4) and counterelectrode (3).

2. Process according to Claim 1, characterized in that the direct voltage (V_{dc}) at least corresponds to the deposition potential of the catalytically active material (6, 6.1).

3. Process according to Claim 1, characterized in that the substrate (4) is provided, on its surface (4.1) which is to be coated, with a predetermined surface roughness prior to the deposition.

4. Process according to Claim 3, characterized in that the surface roughness is in the range from 0.3 µm to 10 µm.

5. Process according to Claim 1, characterized in that the catalytically active material (6) is deposited as substantially spherical metal clusters (6.1) as a result of the alternating voltage component (V_{ac}) being applied with a frequency of over 50 Hz.

6. Process according to Claim 1, characterized in that the catalytically active material (6) is deposited as substantially dendritic metal clusters (6.1) as a result of the alternating voltage component (V_{ac}) being applied with a frequency of between 5 and 50 Hz.

7. Process according to Claim 1, characterized in that the catalytically active material (6) used is a precious metal or a mixture of precious metals and/or catalytically active materials.

8. Process according to Claim 1, characterized in that substantially spherical platinum clusters are deposited on a stainless steel substrate from a solution of a platinum compound in 0.1 M H_2SO_4 with a platinum content of approximately 0.1 g/l as a result of a modulated voltage comprising a direct voltage (V_{dc}) of approximately 1.3 volts superimposed with an alternating voltage (V_{ac}) with a voltage swing (V_{PP}) of 0.3-1 volt and a frequency of 50-100 Hz being applied between stainless steel substrate (4) and counterelectrode (3).

9. Process according to Claim 1, characterized in that substantially dendritic platinum clusters are deposited on a stainless steel substrate from a solution of a platinum compound in 0.1 M H_2SO_4 with

a platinum content of approximately 0.1 g/l as a result of a modulated voltage comprising a direct voltage (V_{dc}) of approximately 1.3 volts superimposed with an alternating voltage (V_{ac}) with a voltage swing (V_{PP}) of 0.3-1 volt and a frequency of 5-15 Hz being applied between stainless steel substrate (4) and counterelectrode (3).

10. Process according to Claim 1, characterized in that substantially dendritic rhodium clusters are deposited on a stainless steel substrate (4) from a solution of a rhodium compound in 0.1 M H_2SO_4 with a rhodium content of approximately 0.2 g/l as a result of a direct voltage (V_{dc}) of 1.4-1.6 volt being applied between stainless steel substrate and counterelectrode (3) and an alternating voltage (V_{ac}) with a voltage swing (V_{PP}) of 0.3-1.5 volts and a frequency of 5-15 Hz being superimposed.

11. Process according to Claim 8 or 9, characterized in that the size of the platinum clusters is between 2 nm and 1 µm.

12. Process according to Claim 1, characterized in that the counterelectrode (3) is formed by platinum-coated titanium.

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(1/5)

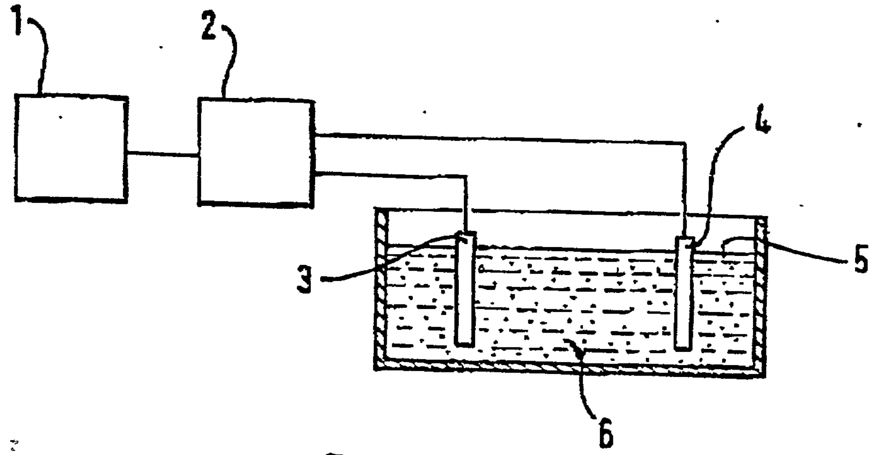

Fig. 1

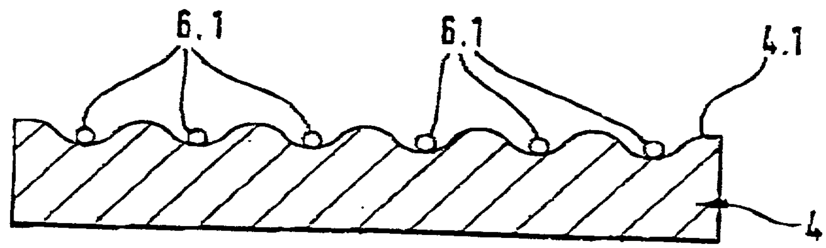

Fig. 2

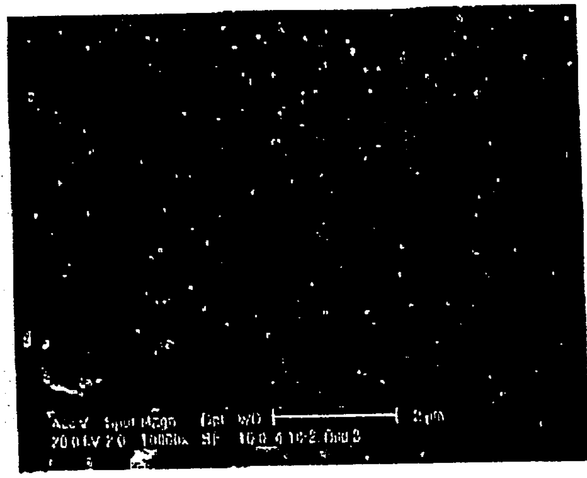

Fig. 3a

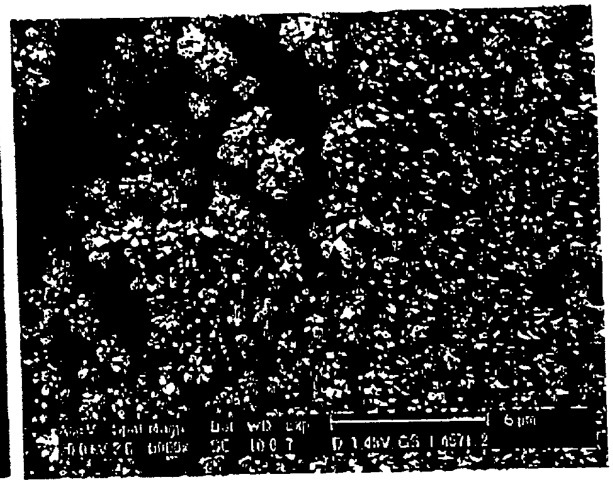

Fig. 3b

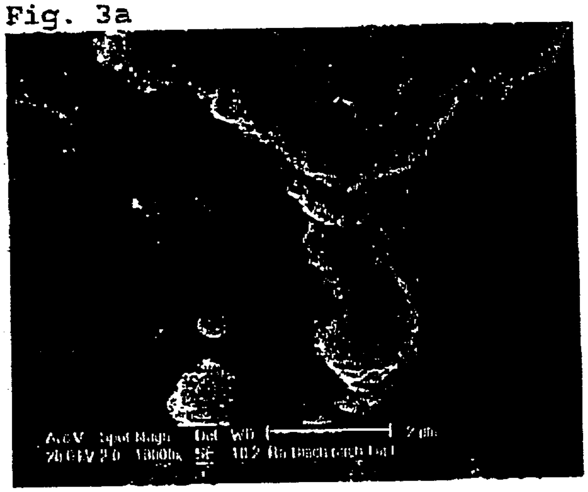

Fig. 3

Fig. 3c

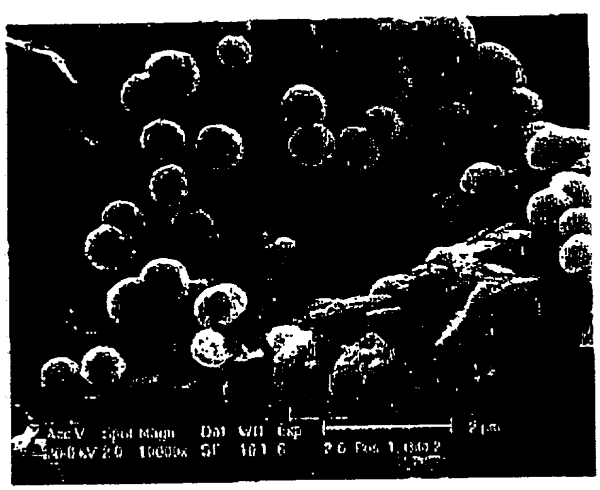

Fig. 4

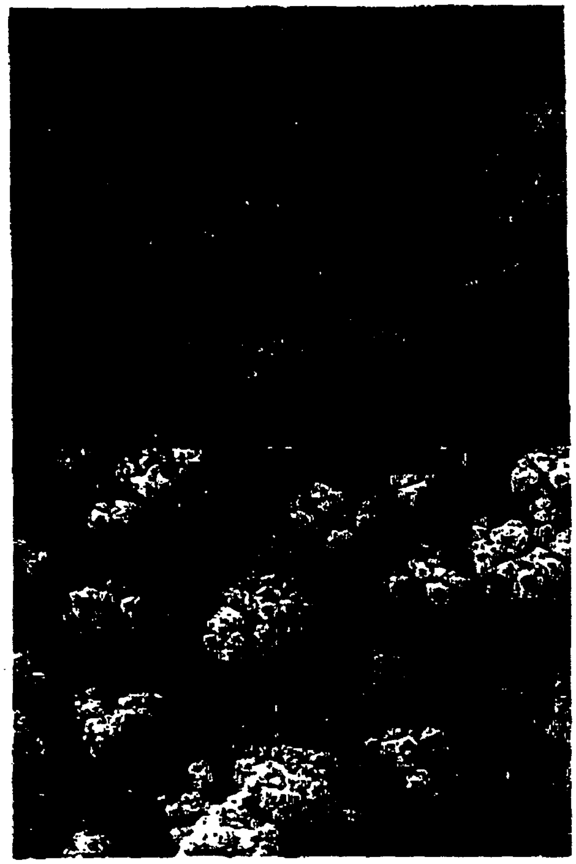

Fig. 5a

Fig. 5b

Fig. 5

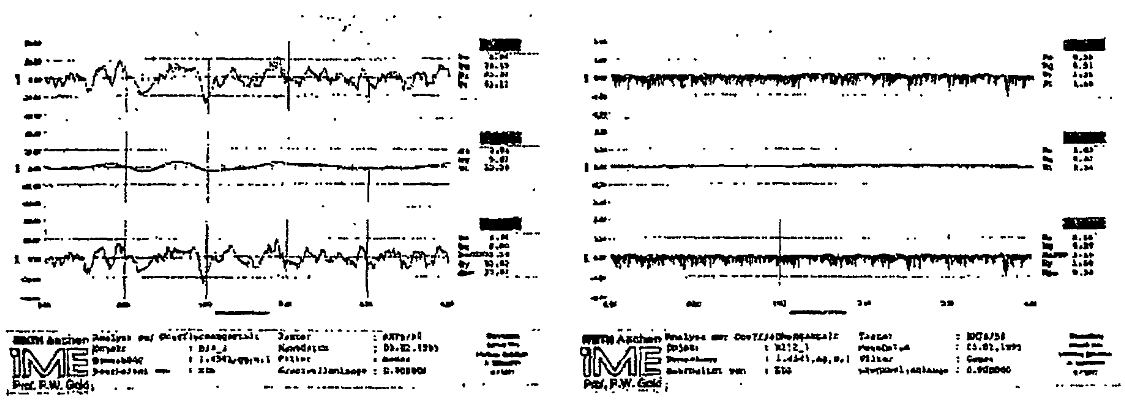

Fig. 6a

Fig. 6b

Fig. 6

(4/5)

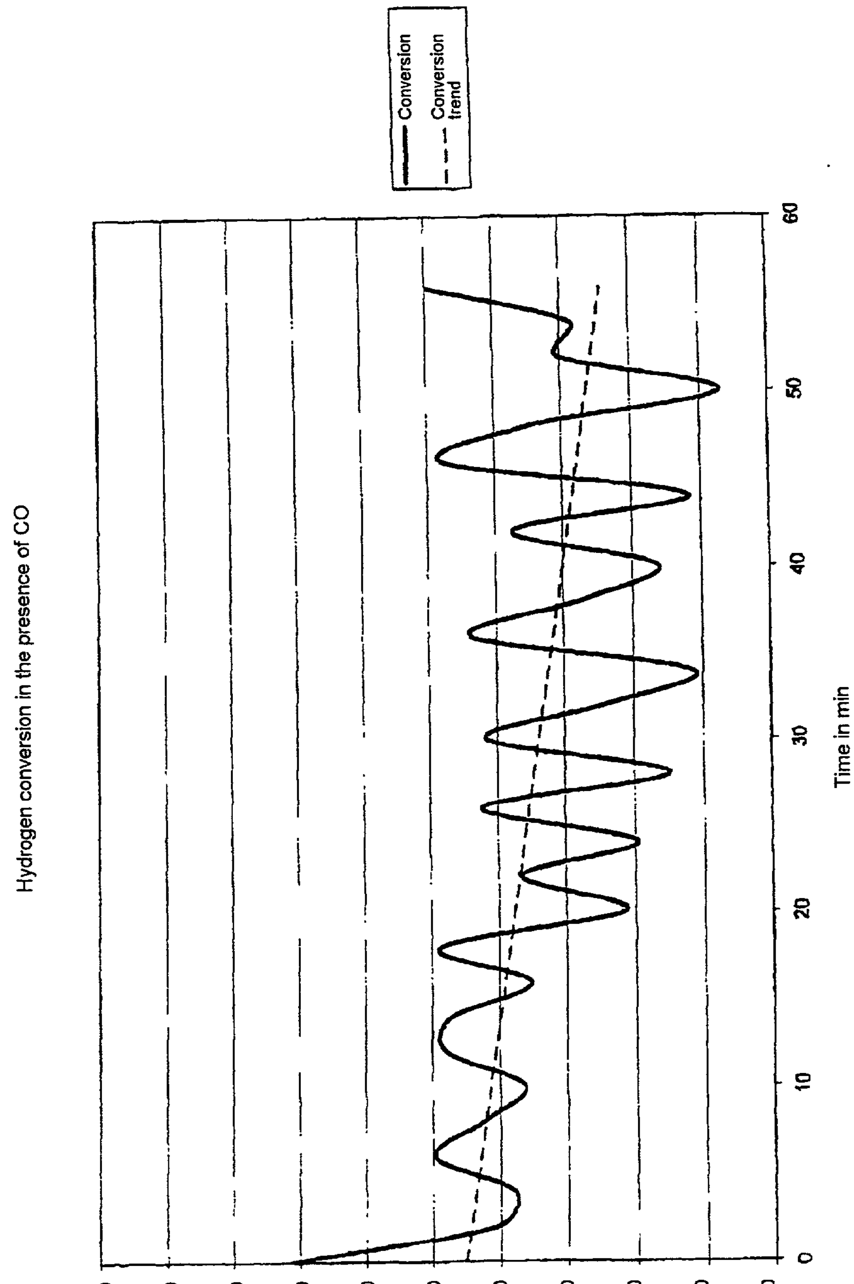
Hydrogen conversion in the presence of CO
Conversion
Conversion trend
Conversion in %
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
10
20
30
40
50
60
Time in min

Fig. 7

(5/5)

Conversion rates achieved in the long-term test

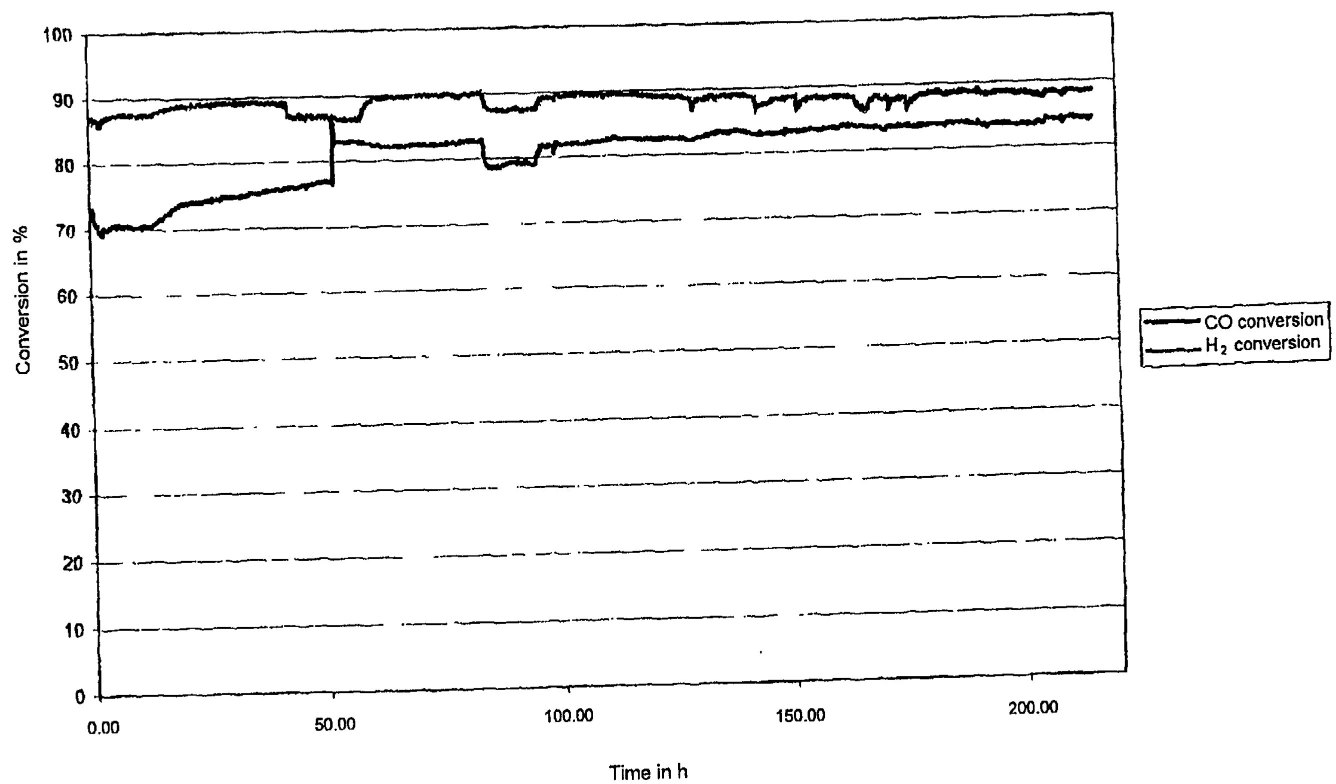

Fig. 8

P033547

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (includes Reference to PCT International Applications)	ATTORNEY'S DOCKET NUMBER 225/50412

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR PRODUCING A CATALYTIC CONVERTER

the specification of which (check only one item below):

[ ] is attached hereto.

[ ] was filed as United States application
Serial No.
on
And was amended
on _______________ (if applicable).

[X] was filed as PCT international application
Number PCT/EP00/01914
on March 4, 2000
and was amended under PCT Article 19
on _______________ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations. §1.56(a).

I hereby claim foreign priority benefits under Title 35, United State Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Germany	199 12 896.0	23 March 1999	[x] Yes [ ] No
			[ ] Yes [ ] No
			[ ] Yes [ ] No
			[ ] Yes [ ] No
			[ ] Yes [ ] No

Combined Declaration For Patent Application and Power of Attorney (Continued) (includes Reference to PCT international Applications	ATTORNEY'S DOCKET NUMBER 225/50412

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application:

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U.S. APPLICATIONS			STATUS *(Check one)*		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (IF ANY)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

Herbert I. Cantor, Reg. No. 24,392; James F. McKeown, Reg. No. 25,406; Donald D. Evenson, Reg. No. 26,160; Joseph D. Evans, Reg. No. 26,269; Gary R. Edwards, Reg. No. 31,824; Jeffrey D. Sanok, Reg. No. 32,169; and Richard R. Diefendorf, Reg. No. 32,390.

Send Correspondence to: Crowell & Moring, L.L.P.. P.O. Box 14300 Washington, D.C. 20044-4300	Direct Telephone Calls to: *(name and telephone number)* (202) 624-2500

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	FULL NAME OF INVENTOR 2-00	FAMILY NAME BRITZ	FIRST GIVEN NAME Peter	SECOND GIVEN NAME
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS Martinstrasse 18, 89134	CITY Blaustein	STATE & ZIP CODE/COUNTRY Germany

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201	SIGNATURE OF INVENTOR 202	SIGNATURE OF INVENTOR 203
07.12.01 [signature]	19.12.01 Peter Britz	23.10.01 Ellen Dahlhoff
DATE	Date	DATE

Combined Declaration For Patent Application and Power of Attorney (Continued) (includes Reference to PCT international Applications	ATTORNEY'S DOCKET NUMBER 225/50412

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U.S. APPLICATIONS			STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (IF ANY)			

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	POST OFFICE ADDRESS	POST OFFICE ADDRESS ~~Watzmannstrasse 20, 71067~~ Hambergweg 30, 71120	CITY ~~Sindelfingen~~ Grafenau	STATE & ZIP CODE/COUNTRY Germany

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 204	SIGNATURE OF INVENTOR 205	SIGNATURE OF INVENTOR 206
Wolfgang Hölderlich	[signature]	Gabriele Stäb
DATE 07.01.2002	Date 26.11.2001	DATE 2001-11-15

Combined Declaration For Patent Application and Power of Attorney (Continued) (includes Reference to PCT international Applications	ATTORNEY'S DOCKET NUMBER 225/50412

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PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (IF ANY)			

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207	FULL NAME OF INVENTOR 1-00	FAMILY NAME URBAN	FIRST GIVEN NAME Peter	SECOND GIVEN NAME
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208	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
209	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
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SIGNATURE OF INVENTOR 207	SIGNATURE OF INVENTOR 208	SIGNATURE OF INVENTOR 209
Peter Urban		
DATE 22.01.2002	Date	DATE

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